

PRESSURIZED CONTAINERS AND METHOD FOR MAKING THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application Serial No. 60/450454 filed on February 26, 2003, which is incorporated herein by reference in its entirety.

5 [001] The present invention relates to pressurized containers or vessels made from reinforced thermoplastics and methods for making pressurized containers or vessels from reinforced thermoplastics.

BACKGROUND OF THE INVENTION

10 [002] There has been a growing interest in using plastics for pressurized containers, primarily for containing beverages, but increasingly for other utilities such as containers to dispense either gaseous or liquid carbon dioxide for use in pneumatic power devices such as garden pressure sprayers, power tools, etc. wherein the high pressure carbon dioxide provides mechanical power. There is also an increased interest in the use of plastic containers in applications such as fire extinguishers, cylinders containing medical gases for distribution in laboratories and larger (e.g. 5 to 50 liters capacity), and cylinders such as those used in the distribution of oxygen, nitrogen, carbon dioxide and
15 the like to industrial users.

[003] For use in beverage container applications, U.S. Patent No. 3,712,497 discloses bottles formed of thin walled, flexible synthetic plastics, in separate parts which are later friction welded together forming the bottles, capable of withstanding internal pressures of up to 75 psi.

20 [004] Also for beverage containers, U.S. Patent No. 4,591,066 discloses a unitary molded plastic body for containing pressurized liquid beverage made out of polystyrene, PET, or polypropylene. However, in packaging draft beer in containers as disclosed herein, it is found that these containers are quite permeable to carbon dioxide. Generally, when used for beer storage and with the migration of carbon dioxide through
25 the plastic membrane / wall being temperature related (higher at room temperature than at 30-32oF), beer stored in the plastic containers of the prior art will have lost so much of its carbon dioxide content after a few days that the remaining beer will no longer be palatable and flat-tasting. EP 0 578 711B1 discloses an improved container for beer and

other beverages in the form of a layered construction of at least two plastic materials, with the plastic materials being arranged in adjacent layers fastened together, or being laminated together. The improved container herein can withstand pressure of up to approximately 420kPA or about 65 psi. In one embodiment of the container, the first plastic material is a polyethylene terephthalate, and the second plastic material is nylon.

[005] Applicants have found that the use of reinforced polyesters in pressurized containers offers a package with gas and moisture barrier properties as well as excellent physical properties in terms of minimal creep or dimensional changes from the effects of pressure in storage or usage, as well as sufficient impact strength for safety in storage and handling.

SUMMARY OF THE INVENTION

[006] The invention relates a pressurized container made of reinforced polyesters having sufficient creep resistance, impact strength, CO₂ and O₂ barrier resistance, wherein upon being filled with a liquid having a dissolved carbon dioxide content of in the range of 0.4 – 0.6 wt % at an internal pressure of at least 1 bar, said pressurized container maintains a dissolved carbon dioxide content of at least about 0.25 wt % after 6 months at a storage temperature of about 30 to 35 °C, and an O₂-permeation of less than 1.0 ppm.

[007] The invention also relates to the use of long-glass fiber reinforced polyesters in pressurized containers for excellent creep resistance, impact strength, water and CO₂ / O₂ barrier properties.

DETAILED DESCRIPTION OF THE INVENTION

[008] Applicants have found that reinforced plastic materials, i.e., polyesters reinforced with various materials, e.g., long-glass fibers and the like, provide a combination of excellent barrier and physical properties such as low permeability to gases, high strength, and low creep at elevated temperatures, thus excellent for packaging applications such as pressurized containers for beverages, foodstuff, and the like.

[009] Reinforced Thermoplastic Materials for the Containers. The polyester resins utilized in this invention include, in general, linear saturated condensation products of diols and dicarboxylic acids, or reactive derivatives thereof. Polyesters are well known as film and fiber formers, and they are manufactured by methods known in the art including those disclosed in U.S. Pat. Nos. 2,465,319 and 3,047,539.

[010] In one embodiment, the polyesters comprise condensation products of aromatic dicarboxylic acids and aliphatic diols. In another embodiment, the polyesters are poly(1,4-dimethylol cyclohexane dicarboxylates, e.g., terephthalates). In addition to phthalates, small amounts of other aromatic dicarboxylic acids, such as isophthalic dicarboxylic acid, naphthalene dicarboxylic acid, or aliphatic dicarboxylic acids, such as adipic acid, can also be present in the resins. The diol constituent can likewise be varied, in some embodiments, by adding small amounts of cycloaliphatic diols.

[011] In one embodiment, the polyesters comprise a poly(alkylene terephthalate, isophthalate or mixed isophthalate-terephthalate, e.g., up to 30 mole percent isophthalate), with the alkylene groups containing from 2 to 10 carbon atoms, e.g., poly(ethylene terephthalate) ("PET") or poly(1,4-butylene terephthalate) ("PBT"). In yet another embodiment the polyester resins may comprise entirely of PET, PBT, or a combination thereof. In one embodiment, the polyesters comprise a mixture of PBT to PET at a weight ratio of about 1:1 to about 20:1.

[012] In one embodiment, the poly(1,4-butylene terephthalate) resin used is one obtained by polymerizing a glycol component at least 70 mol %, preferably at least 80 mol %, of which consists of tetramethylene glycol and an acid or ester component at least 70 mol %, preferably at least 80 mol %, of which consists of terephthalic acid, and polyester-forming derivatives therefore.

[013] In another embodiment, the polyester is a poly(1,4-butylene terephthalate) homopolyester. In yet another embodiment, copolyesters are used. These comprise at least about 70 mole percent, based on total monomer content, of butylene and terephthalate units. The comonomer may be either a dicarboxylic acid or diol or a combination of the two. Suitable dicarboxylic acid comonomers include the C₈ to C₁₆ aromatic dicarboxylic acids, including the benzene dicarboxylic acids, i.e. phthalic and isophthalic acids and their alkyl, e.g. methyl, derivatives and C₄ to C₁₆ aliphatic and cycloaliphatic dicarboxylic acids including, for example, sebacic acid; glutaric acid; azelaic acid; tetramethyl succinic acid; 1,2-, 1,3- and 1,4-cyclohexane dicarboxylic acids and the like. Suitable diol comonomers include but are not limited to C₂ to C₈ aliphatic and cycloaliphatic diols, e.g. ethylene glycol, hexanediol, butanediol and 1,2-, 1,3- and 1,4-cyclohexanedimethanol.

[014] In one embodiment, the polyester resin having a coefficient of thermal expansion (CTE) higher than that of the intended reinforcing material used, so that the

polyester material shrinks around the reinforcing material causing compressive stresses which grip the reinforcing material in place.

5 [015] In another embodiment of the present invention, the polyesters may be blended with a polycarbonate resin. Polycarbonate resins useful in preparing the blends of the present invention are generally aromatic polycarbonate resins.

[016] Optional Additives to the Polyester Resin Matrix. In one embodiment of the invention, the polyesters may be modified with additives such as a high molecular weight polyetherimide base material (e.g. an polyetherimide ester elastomer) as a warpage control additive.

10 [017] In another embodiment of the invention wherein the polyester is PBT, additives such as (co-)polyolefins or polyethylenes are added for improved impact strength. In one example, the impact strength additive is selected from ethylene-vinyl acetate (EVA), linear low-density polyethylene (LLDPE), and alpha-olefin-glycidyl methacrylate copolymers and terpolymers.

15 [018] In yet another embodiment of the invention wherein the weight ratio of polyester to the reinforcing agent is equal to or below about 2.25, a copolymer or interpolymer comprising glycidyl 2-alkenoates and alpha-olefins is added to the polyester for improved impact strength and improved melt viscosity to facilitate the construction of the finished pressurized containers.

20 [019] In another embodiment, the polyesters may further contain one or more conventional additives such as, for example, antioxidants, carbon black, reinforcing agents, plasticizers, lubricity promoters, color stabilizers, ultraviolet absorbers, X-ray opacifiers, dyes, pigments, fillers including mineral fillers, mold release agents such as polyethylene, and the like.

25 [020] In one embodiment, mineral fillers include alumina, amorphous silica, anhydrous aluminum silicates, feldspar, talc, milled glass, phenolic resins, glass microspheres, metal oxides such as titanium dioxide, zinc sulfide, ground quartz, clays such as hydrated aluminum silicate, and the like are used in the polyester matrix.

30 [021] In yet another embodiment, thermal, oxidative and/or ultraviolet stabilizers comprise phenols and their derivatives, amines and their derivatives, compounds containing both hydroxyl and amine groups, hydroxyazines, oximes,

polymeric phenolic esters and salts of multivalent metals may be optionally added to the polyester resins.

5 [022] Reinforcing Agents for the Polyester Resin Matrix. In one embodiment, the reinforcing agents are fibers in the form of fiberglass, carbon or aramid fibers in roving, woven fabric form, or in combination of fiberglass and carbon or aramid fibers. In another embodiment, the reinforcing agents are metals drawn into wire or filaments, or polyamide polymers characterized by the presence of the amide group -CONH . In yet another embodiment, the reinforcing agents are solely glass fibers available in roving, continuous strand mat, and stitched rovings (0° , 90° , and $\pm 45^\circ$ orientations).

10 [023] In one embodiment, the fibers are precoated with a binder to enhance compatibility with the polyester resin matrix. The coating can comprise normal fiberglass coating materials: polyurethane resin, polyacrylate resin, polyester resin, polyepoxide resin, and functional silanes, especially epoxy or amine functional alkoxy silanes. The amount of the coating agent employed is generally that amount which is
15 sufficient to bind the filaments into a continuous strand. Generally, this may be about 1.0 weight percent based on the weight of the glass filament.

 [024] The fiber diameters typically range from about 3 to 50 microns. In another embodiment, the filaments in the form of glass fibers have a diameter of about 5 to 30 microns. In yet another embodiment, the fiber has a diameter of about 10 to 20 microns.

20 [025] In embodiment of fibers as reinforcing agents, the fibers in the form of chopped fiberglass strands have a length of about $1/8''$ to about $1''$. In another embodiment, long-fibers with lengths of more than $1''$ are used, for increased strength and moldability of the containers. In yet another embodiment, the fiberglass fibers are comprised of lime-aluminum borosilicate glass that is relatively soda free. This is known
25 as "E" glass. In other embodiments, other glasses are used as well e.g., the low soda glass known as "C." In another embodiment, glass filaments known as G-filaments are used.

 [026] The glass filaments are made by standard processes, e.g., by steam or air blowing, flame blowing and mechanical pulling. In one embodiment, the filaments are
30 made by mechanical pulling. In one embodiment, the filaments are in the form of being bundled into fibers and the fibers bundled in turn to yarns, ropes or rovings, for final use in reinforcing the polyesters for use in the pressurized containers of the invention.

[027] In one embodiment of the invention, the reinforcing agents comprise a range of materials other than glass fibers and in the form other than filaments, e.g., microspheres. These include but are not limited to glass, ceramic materials such as graphite, wollastonite, carbons, metals, e.g., aluminum, iron, nickel, stainless steel and the like, titanates, e.g., titanate whiskers, quartz, clay, mica, talc, mixtures of the foregoing and the like. The metal and metal glass fiber materials that can be used include those disclosed in the U.S. Pat. No. 4,525,314, the entire disclosure of which is incorporated herein by reference. The ceramic materials from which the reinforcing fibers can be made include silicon carbide, silicon nitride, carbon, graphite and aluminum oxide. The metal, ceramic, and glass microspheres than can be used as reinforcing agents include those disclosed in U.S. Pat. No. 4671994, the entire disclosure of which is incorporated herein by reference.

[028] In one embodiment, reinforcing agents are used in an amount ranging from about 5 to about 60 weight percent based on the total weight of the thermoplastic blend composition. In another embodiment, the concentration of the reinforcing agents is expressed as volume %, and ranging from about 1 to about 50 volume % (vol. %). The volume percent can be calculated by comparing the total area of the cross section of a finished part with the cross sectional area of the fibers. In another embodiment, this amount is less than about 40 vol. %. In a third embodiment, it is less than 30 vol. %. In a fourth embodiment, it is about 5 to 20 vol. %.

[029] Processing of the Reinforced Polyesters / Forming the Pressurized Containers. In one embodiment of the invention, wherein the reinforcing agents used are long fibers, a pultrusion process known in the art is used to form the components into shape. In a pultrusion process, the long glass fiber material is drawn through a bath containing the polyester resins plus any additives. In one embodiment of the pultrusion process, the long glass fiber material is first impregnated with the polyester resin of the invention (plus any optional additives). Laminate formed is pulled through a heated die controlled to precise tolerances depending on the final container application specifications. The finished product is cut and tooled into various parts of the container, e.g., sidewall, top or bottom part and the like. The parts are subsequently welded forming the finished containers.

[030] In yet another embodiment, a process as generally described in EP 0 820848B1 is used for a lineal structure particularly useful for a tall pressurized container, which reference is expressly incorporated herein. This process comprises feeding the melted polyester materials of the invention into a die having an inlet for receiving the

melted material, and an outlet having a geometry corresponding to the desired part of the container of the invention. The outlet is positioned downstream from the inlet wherein the melted polyester resin flows from the inlet to the outlet. A plurality of fiber bundles are introduced to the stream at predetermined spaced apart radial positions for providing the fiber reinforcement to the lineal profile. The fiber bundles extend in the longitudinal direction at predetermined locations in the profile. The finished product is cut and tooled into various parts of the container, e.g., sidewall, top or bottom part and the like.

[031] Subsequent to the pultrusion or extrusion process forming the parts, and the assembling of the parts via welding or other processes known to the art to form the finished containers, the containers can be further reinforced with additional bands of materials at generally taught in EP0852695B1 for "Blast Resistant And Blast Directing Containers." In one embodiment, the pressurized container further comprises a plurality of spaced, substantially parallel composite strips attached to and reinforcing the container with each strip being a tape of unidirectional high strength fibers or oriented film encircling the container in a hoop direction at least once.

[032] In another embodiment of the invention, chopped glass strands are used as reinforcing agents. The chopped glass strands may be first blended with the polyester resin and then fed to an extruder and the extrudate cut into pellets. In another example, they may be separately fed to the feed hopper of an extruder to preparing reinforced polyester pellets. The pellets so prepared when cutting the extrudate may be one-fourth inch long or less. The dispersed glass fibers are reduced in length as a result of the shearing action on the chopped glass strands in the extruder barrel.

[033] The reinforced polyester resins are subsequently shaped into pressurized containers or parts thereof, via common processes known in the art, such as extrusion blow molding, injection blow molding, profile extrusion, pipe extrusion, co-extrusion, extrusion coating, foam molding, foam extrusion, thermoforming, and the like. The parts can be subsequently welded to form the finished pressurized containers.

[034] Properties of the Pressurized Containers. In one embodiment of the invention, wherein the reinforced polyester pressurized containers of 2-4 mm thickness are used as beer containers, i.e., beer kegs, it is found that the reinforced polyester pressurized containers of the invention have inherently low CO₂ and oxygen permeation properties, wherein upon being filled with a liquid having a dissolved carbon dioxide content of 0.4 – 0.6 wt % at an internal pressure of at least 1 bar, said pressurized

container maintains a dissolved carbon dioxide content of at least 0.25 wt % after 0.5 year at a storage temperature of about 30 to 35 °C and an O₂-permeation of less than 1.0 ppm.

5 [035] With respect to creep properties, in one embodiment of the invention, the pressurized containers, made out of reinforced polyesters, used at an initial internal pressure of 1-5 bar have a creep < 3 % after 0.5 year at room temperature.

[036] With respect to impact break resistance properties, in embodiments wherein long-glass-fibers are used as reinforcing agents and pultrusion technology is used to fabricate the pressurized containers of the present invention, tests on a number of differently designed and produced 15 liter vessels of 2-4 mm thickness show that
10 pressurized containers (50% filled and 80 % filled) are break-resistant upon being dropped from heights ranging from 0.45 – 1 m.

[037] In food applications, e.g., as beer kegs or pressurized containers for soft drinks and a variety of foodstuffs, it is found that the reinforced polyesters containers of the present invention do not import unacceptable levels flavoring changes to the products.

15 [038] EXAMPLE. The examples below are merely representative of the work that contributes to the teaching of the present application.

[039] Examples 1 - 4. In this example, reinforced polyester compositions comprising of PBT (poly(butylene terephthalate) with molecular weight of appr. 80,000 (as expressed as PS molecular weight), 0.15 % Irganox 1010 as a stabilizer,
20 approximately 1 % of a polyethylene as release agent., and from 30 to 50 wt. % of glass fiber.

[040] The compositions are referred to as 30% SGF, 50% LGF, 30% LGF, and 50% LGF, depending on whether short glass or long glass fiber is used. The short glass fiber is in the form of E-glass chopped strands commercially available from NEG as T-120. The long glass fiber (e.g. E-glass based) can be treated with a finishing agent such
25 as a silane-based coupling agent, greige goods such as urethane-based resins or epoxy-based resins, a thermal stabilizer such as typically phosphite-based resins, or any other adequate surface-treating agents depending upon aimed uses, if required.

[041] The LGF compositions are made according to the pultrusion process as
30 generally disclosed in U.S. Patent No. 4,559,262, the entire disclosure of which is incorporated herein by reference. In the examples, PBT polymer melts are prepared in a bath of about 260°C. Fiber glass filaments (in the form of a glass roving) are pulled

through the molten polymer over one spreader bar situated in the bath at a rate of 30 cm/minute, giving a dwell time in the bath of 30 seconds. The impregnated roving is pulled through a 3 mm diameter die in the wall of the bath and then cooled, for a completely wetted material. The amount of PBT in the finished product (for 30 or 50 wt. % concentration of fiber) is controlled by the length of the path over which the fiber band contacts the heated spreader surface.

[042] The products obtained by the continuous pultrusion are subsequently chopped to form pellets having a length in the range of at least 5–10 mm. The used LGF products are supplied by LNP under the name of Verton AF 7006 (30 % LGF) and WF 700 10 (50 % LGF).

[043] The SGF blends are made by dry blending of ingredients with exception of the glass fiber. The blends are subsequently compounded on a WP25 mm co-rotating extruder, where the glass is separately fed down-stream the extruder. The melt temperature was approx. 250-260°C and at RPM of 300. The products obtained are extrudated to form pellets.

[044] The SGF and LGF products are molded into samples using an Engel 75 tons machine with a temperature setting of 240-260 C (from throat to nozzle) and a mold temperature of 60 C. Prior to molding the pellets were predried at 120 C for 2 hours.

[045] The properties of the short-glass fiber (SGF) and long-glass fiber (LGF) samples in Examples 1-4 are measured according to the following procedures:

Notched Izod (NI) and Unnotched Izod (UNI): This test procedure is based on the ISO180 method, with the notched (INI) and the unnotched (UNI) impact strengths being obtained by testing a notched or unnotched specimen. The results of the test is reported in terms of energy absorbed per unit of specimen width, and expressed in kilojoules per square meter (kJ/m²). Typically, the final test result is calculated as the average of test results of five test bars.

The Flexed Plate Impact Test: This test procedure is used to determine maximum force, energy at max, and energy at break and deflection at break, based on the ISO6603 method and used at different speeds.

Type	Max.Force (N) @ 4 m/s	Max.Force (N) @ 0.1 m/s	Energy @ Max (J) @ 4 m/s	Energy @ Break (J) @ 4 m/s	Defl. @ Brk (mm) @ 4 m/s	INI (kJ/m2) acc. LNP	INI (kJ/m2) acc. GEP	UNI (kJ/m2) acc GEP
50% SGF	2526	2780	8.1	13.8	10.4	13.4	14.1	45.9
50% LGF	2834	2741	8	17.9	15.1	40	42.1	59.2
30% LGF	2656	2519	9.5	15.9	11.9	30	32.5	56.2
30% SGF	2292	2365	9.3	12.1	12.8		9.9	48.9

[046] Example 2. In this example, the 50% LGF composition in Example 2 is used in a fiber-reinforced polyester pressurized vessel. i.e., beer kegs, with a pultrusion process is used to form the components of the beer kegs.

5 [047] The beer kegs are filled from beer tanks at suitable internal pressure of about 2 bars and at temperature of about 20 to 35 °C, and with the beer having a dissolved carbon dioxide content of about 0.5 wt %.

10 [048] After a shelf life of approx. six months and at a temperature of 20 to 35 °C, it is found that the beer in the fiber-reinforced polyester beer kegs of the present invention has a dissolved carbon dioxide content of at least 0.25 wt. %. It is also found that the beer is not flat when dispensed and consumed. It is also found that after the beer is partially consumed and in storage in the keg at about 20 to 35°C for two to three days, the remaining beer still contains a dissolved carbon dioxide volume of about 0.25 wt %. Additionally, the beer also retains a palatable taste and is not flat, all without the need for
15 any external pressure source.

[049] It should be understood that the foregoing description is only illustrative of the invention. Various alternative modifications can be employed by those skilled in the art without departing from the scope of the invention. Accordingly, the present invention is intended to embrace all such alternative, modifications and variances, which fall within the scope of the appended claims.